

ASPHALTENE AND RESID PYROLYSIS 2: THE EFFECT OF REACTION ENVIRONMENT ON PATHWAYS AND SELECTIVITIES.

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Keywords

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Abstract

Resids and isolated asphaltenes from four feedstocks were pyrolyzed at temperatures of 400, 425 and 450 °C for holding times ranging from 20 to 180 minutes in micro-batch reactors. Reaction products were recovered as gas, maltene, asphaltene and coke lumps. The maltene, asphaltene and coke product fractions were collected by a solvent extraction sequence where heptane-soluble material was defined as maltene, toluene-soluble material as asphaltene, and toluene-insoluble material as coke. Gas chromatography revealed the presence of C₁-C₅ paraffins, C₂-C₅ olefins, isoparaffins, H₂S and CO₂.

Results were summarized by a lumped reaction network which allowed for quantitative kinetics. Comparison of relative kinetics and apparent activation energies yielded insight into thermal reaction pathways, feedstock effects, and asphaltene environment effects. At 400°C and 425°C, isolated asphaltene reacted selectively to maltenes. At 450°C asphaltene reacted predominately to coke. Isolated maltene pyrolysis indicated that asphaltene and coke formed in series, i.e., M→A→C.

Introduction

The increased usage of heavy petroleum feedstocks has focused attention on problems associated with the refining of heavy feedstocks, such as solids formation and catalyst deactivation. On a feedstock structural level, these problems are associated with high aromaticity, high molecular weight, and high heteroatom content¹.

Asphaltene is the aromatic-soluble and paraffinic-insoluble fraction of crude oil. Understanding the effects of environment on asphaltene reaction pathways can provide insight into the processing problems of heavy crudes. Previous asphaltene and resid thermal pyrolysis studies² have yielded information on environmental and feedstock effects. The current work is an extension of that study. Arabian Heavy Resid (AHR) and Arabian Light Resid (ALR) were subject to pyrolysis in an isothermal sand bath at 400, 425, and 450°C for holding times between 20 and 180 minutes. The isolated maltene from ALR was also pyrolyzed at 425°C. Gaseous products were collected and analyzed by GC. A soxhlet sequence was used to separate maltene, asphaltene and coke. The time dependence of the product distributions was used to calculate lumped kinetic rate constants. Arrhenius parameters were calculated for each network step.

Experimental Methods

1) Samples

Asphaltenes were precipitated from the resids at a weight ratio of 40/1, n-heptane to resid. The mixture was stirred for 1 hr at 60 °C, and then allowed to cool under continuous stirring for 4 hr. The solution was then allowed to settle overnight prior to filtering. Maltenes were collected by evaporating the n-heptane from the filtrate. The asphaltene was subject to soxhlet extraction to verify the absence of maltenes.

The samples were characterized by elemental analysis, simulated distillation, proton NMR, SARA (saturate, aromatic, resin, asphaltene) and molecular weight by VPO. Molecular weight experiments were carried out at 130°C in nitrobenzene. Molecular weights were extrapolated from measurements at three concentrations. The results are given in Table (I). VPO measurements showed that Maya isolated asphaltene and Arabian Heavy resid had the highest molecular weight in their respective classes. Elemental analysis indicated that heteroatoms were concentrated in the asphaltene fraction. Simulated distillation analysis revealed some variability in cut point for the resids.

2) Pyrolysis Reactions

Reactions were carried out in micro-batch reactors. Briefly, a glass tube containing the sample was loaded into the reactor. It was purged several times with high pressure nitrogen to minimize potential oxidation reactions then reacted in an isothermal sandbath. Reaction products were separated into gas, maltene, asphaltene and coke fractions. Gas products were collected and then analyzed by gas chromatography equipped with a thermal conductivity detector and a 6 ft propak Q column. Maltene, asphaltene and coke fractions were collected by a soxhlet extraction sequence. The yield of each fraction was calculated gravimetrically.

Results and Discussions

1) Isolated asphaltenes

Figures (1a-c) show the kinetics of pyrolysis of isolated asphaltenes. The curves drawn through experimental data represent a first-order model fit. Asphaltene reactivities were as follows: AH~AL~H>M at 400 and 425°C. At 450°C asphaltene conversion was extremely rapid.

2) Asphaltene in resid

Figures (2a-c) depicts the time dependence of the ratio of the weight of asphaltene to initial weight of asphaltene in the resid. Clearly the reaction paths of asphaltene are influenced by the resid environment. The amount of AL asphaltene approximately doubled at 400°C. At 425 and 450°C the amount of AL asphaltene rapidly rose to 2-3 times its initial value. Further reaction returned the AL asphaltene amount to a value below this initial level. Asphaltene levels in the other three resids did not increase above the ordinate at any reaction temperatures. Reactivities were as follow: H>AH~M>AL

3) Maltene from isolated asphaltene

Figures (3a-c) summarize the temporal variation of the maltene weight fraction. At 400°C the yield of maltene was nearly the same for all feedstocks. H maltene yield

increased at all temperatures. H had highest maltene yield at 450 °C. M produced the most maltene at 425°C. AH and AL produced the greatest amounts at 400 and 425°C.

The maxima exhibited by all isolated asphaltenes at reaction temperatures of 425 and 450°C are indicative of secondary cracking and possible condensation reactions. The complex behavior is indicative of a chemically complex mixture.

4) Maltene from resids

The temporal variations of the maltene weight fractions for AH, AL, H and M resids are shown in Figures (4a-c). As temperature increased the maltene disappearance rate increased for all resids. After 20 minutes, the disappearance rate of maltenes was similar for all feedstocks.

5) Isolated maltenes and reaction pathways

Experimental results from isolated AL maltenes pyrolysis, as shown in figure (5), suggest that isolated maltenes produced asphaltene and then coke in series. These experiments revealed that the previously proposed pathways² could be simplified since coke was not formed directly from maltene. The network is shown in Figure (6).

Reaction Kinetics

Optimized rate constants for the network of Figure (6) were obtained as described elsewhere.³ Briefly, a simplex minimization program⁴ coupled to the DGEAR⁵ routine minimized the error in the solution of a first-order differential equations developed from figure (6).

The predicted rate constants are shown in Table II. For both isolated asphaltenes and resid, k_4 , the rate constant for the reaction of maltene to gas was negligible. The rate constant for the reactions of asphaltene to maltene and maltene to asphaltene, k_1 and k_5 , were highest for resids. The selectivities, k_1/k_5 , were between 4.5 and 8.6 for four resids at all temperatures.

The activation energies calculated from network parameters for each reaction step are summarized in the table III both for resids and asphaltenes.

Conclusions

- 1) AL, AH and H isolated asphaltenes reacted at the similar rates at 400 and 425°C; The M isolated asphaltene reacted more slowly. All of the isolated asphaltenes reacted at about the same rate at 450°C.
- 2) At 400 and 425°C, the isolated asphaltenes reacted selectively to maltene. At 450°C H isolated asphaltene formed more maltene than M, AL and AH.
- 3) H asphaltene reacted faster than M, AL and AH in the resid at all temperatures. AL asphaltene in the resid reacted most slowly.
- 4) Resids and isolated AL maltene pyrolysis showed that important amounts of asphaltene and coke could be formed by maltenes.

References

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TABLE I

Chemical analysis of Hondo, Maya, Arabian Light, and Arabian resids and their isolated asphaltenes by Elemental, VPO, Proton NMR, Simulated Distillation, ORA, a Soxhlet Extraction techniques (R=resid, A=asphaltene, - =not measured).

Analysis	Hondo (R)	Maya (R)	A. Light (R)	A. Heavy (R)	Hondo (A)	Maya (A)	A. Light (A)	A. Heavy (A)
% Carbon	81.15	85.66	84.41	83.80	80.35	83.08	82.13	82.00
% Hydrogen	9.95	10.41	10.02	9.31	7.96	7.27	7.59	6.69
% Nitrogen	1.01	0.465	0.15	0.44	1.87	1.09	0.75	0.93
% Sulfur	6.90	3.17	4.04	5.31	7.89	7.11	6.17	7.43
% Oxygen	1.02	0.50	0.008	0.020	0.110	0.170	0.036	0.074
% Vanadium	0.017	0.005	0.002	0.007	0.040	0.032	0.010	0.022
% Nickel	0.010	0.005	-	-	-	-	-	-
% Iron	1.47	1.46	1.40	1.33	1.19	1.05	1.11	0.98
H/C	0.011	0.005	0.002	0.005	0.020	0.011	0.008	0.010
N/C	0.032	0.014	0.018	0.024	0.037	0.032	0.028	0.034
S/C	0.009	0.004	0.009	0.013	0.016	0.008	0.013	0.015
O/C								
MW by VPO	862	944	1022	1535	2871	5292	1950	2119
1H NMR	-	-	-	-	20.6	28.1	28.8	29.8
% H (ME)	-	-	-	-	57.6	60.9	44.9	46.7
% H (N + MY)	-	-	-	-	10.6	5.8	12.2	14.8
% H (alpha)	-	-	-	-	11.2	5.2	14.2	9.7
% H (aromatic)	-	-	-	-	-	-	-	-
Simulated Distillation								
%800-1000°F	12.5	19.0	10.1	9.8	-	-	-	-
%1000°F+	87.5	81.0	89.9	90.2	-	-	-	-
ORA								
%Oils	31.7	12.3	-	-	-	-	-	-
%Resins	55.2	71.6	-	-	-	-	-	-
%Asphaltenes	12.5	15.1	-	-	-	-	-	-
Soxhlet Extracted								
%Maltenes	77	88	94	85	-	-	-	-
%Asphaltenes	23	12	6	15	-	-	-	-
SARA								
%Saturates	13	26	30	30	-	-	-	-
%Aromatics	43	51	45	44	-	-	-	-
%Resins	21	11	19	16	-	-	-	-
%Asphaltenes	23	12	6	2	-	-	-	-

Table II

Network Kinetics of the Pyrolysis of Hondo and Maya Resids and their Isolated Asphaltene
(First order units are 1/(hr*wt%))

Rate Parameters.	Hondo Resid	Maya Resid	Arabian Light Resid	Arabian Heavy Resid	Hondo Asphaltene	Maya Asphaltene	Arabian Light Asphaltene	Arabian Heavy Asphaltene
400 °C								
k1	123.62	54.018	2.5800	13.351	0.9369	0.6465	0.7330	48.943
k2	0.3433	0.2689	0.1680	0.3369	3.2014	1.5201	3.0133	2.9273
k3	0.2559	0.1699	0.1390	0.1313	0.4196	0.1503	0.3022	0.3012
k4	0.0025	0.0003	0.0001	0.0003	0.0048	0.0038	0.0000	0.0003
k5	20.044	8.1600	0.3860	2.8021	0.5875	0.6825	0.2540	81.565
425°C								
k1	293.14	115.08	12.757	33.350	2.5700	1.5813	0.9720	114.81
k2	1.4586	0.8568	1.1251	0.8183	3.3700	2.6710	4.3890	6.4369
k3	0.0006	0.3545	0.3565	0.3300	0.5290	0.0010	0.5077	0.7720
k4	0.0765	0.0003	0.0003	0.0005	0.0200	0.4889	0.0000	0.0007
k5	33.910	14.400	2.2291	7.3300	1.1400	0.6977	0.5592	163.81
450°C								
k1	572.53	348.60	34.121	79.350	3.0725	59.438	4.3110	368.58
k2	1.7511	1.4741	1.9663	1.9153	4.2704	203.45	7.3411	13.687
k3	1.1886	0.7349	1.3054	0.9250	1.1481	0.0039	1.5570	2.2512
k4	0.0007	0.0008	0.0007	0.0009	0.0018	0.9305	0.0910	0.0021
k5	97.398	59.571	4.8265	16.380	0.3793	0.4078	9.1011	280.02

Table III

Arrhenius parameters for resids and asphaltenes, (Ea (kcal/mol) , * = not calculated).

Parameters	k1	k2	k3	k4	k5	k1	k2	k3	k4	k5
Hondo Resid					Hondo Asphaltene					
Ea	29.69	31.81	*	*	30.45	23.16	5.53	19.33	*	*
log A	11.74	9.94	*	*	11.48	7.54	2.28	5.86	*	*
Maya Resid					Maya Asphaltene					
Ea	35.98	33.04	28.32	18.80	38.24	86.79	93.82	*	106	*
log A	13.38	10.19	8.42	2.53	13.26	27.79	30.36	*	32.53	*
Arabian Light Resid					Arabian Light Asphaltene					
Ea	50.07	47.88	43.22	42.05	49.07	33.98	17.19	31.58	*	68.74
Log A	16.71	14.87	13.15	9.58	15.58	10.81	6.05	9.68	*	2.16
Arabian Heavy Resid					Arabian Heavy Asphaltene					
Ea	34.47	33.61	37.72	21.22	34.18	38.97	34.57	38.87	38.23	23.89
Log A	12.32	10.44	11.36	3.36	11.55	14.31	11.60	12.08	8.86	9.68

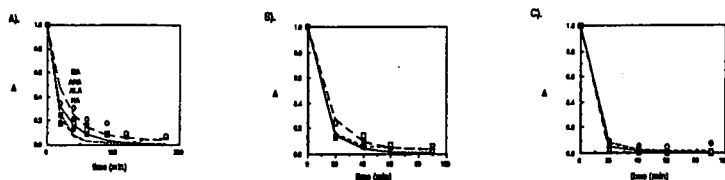


Figure 1. Temporal variation of isolated asphaltene: A) 400°C, B) 425°C, C) 450°C

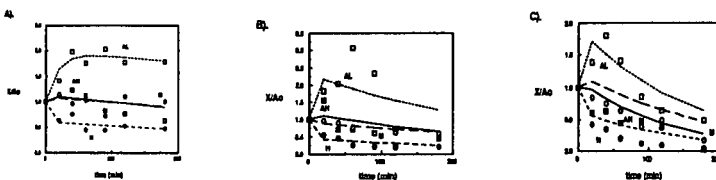


Figure 2. Temporal variation of asphaltene yield in a ratio of asphaltene weight to initial asphaltene weight for resids: A) 400°C, B) 425°C, C) 450°C

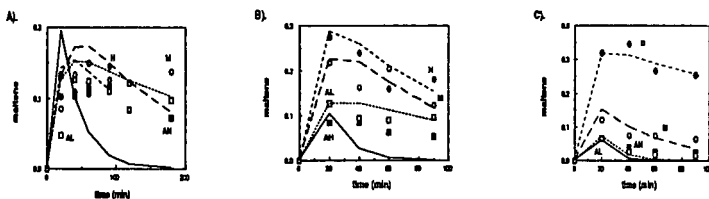


Figure 3. Temporal variation of maltene weight fraction for asphaltenes: A) 400°C, B) 425°C, C) 450°C.

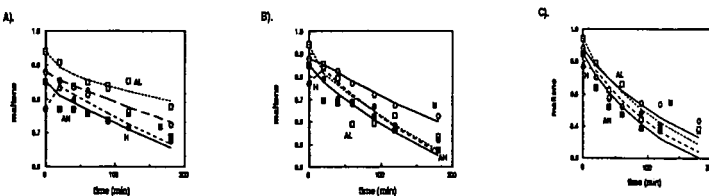


Figure 4. Temporal variation of maltene weight fraction for resids: A) 400°C, B) 425°C, C) 450°C.

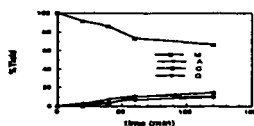


Figure 5. Isolated maltene pyrolysis at 425°C.

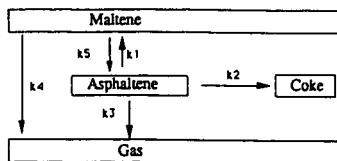


Figure 6. Lumped resid/ asphaltene model